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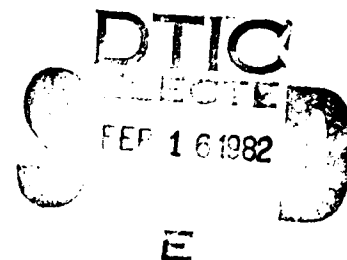
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THESIS

STUDIES OF THE LOW TEMPERATURE HOT
CORROSION OF UNCOATED SUPERALLOYS

by

Garry D. Newberry

September 1981

Thesis Advisor:

Donald H. Boone

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-777091	
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
Studies of the Low Temperature Hot Corrosion of Uncoated Superalloys		Master's Thesis September 1981
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
Garry J. Newberry		
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Postgraduate School Monterey, California 93940		
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Naval Postgraduate School Monterey, California 93940		September 1981
		13. NUMBER OF PAGES
		44
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Marine Gas Turbines, Hot Corrosion, Uncoated Turbine Blade Materials		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
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S/N 0102-014-6601

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This program also showed that the Naval Postgraduate School hot corrosion furnace reproduced the corrosion patterns seen on uncoated alloys in burner rigs and industrial gas turbines.

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Studies of the Low Temperature Hot
Corrosion of Uncoated Superalloys

by

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Lieutenant, United States Navy
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Submitted in Partial Fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

NAVAL POSTGRADUATE SCHOOL
September 1981

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ABSTRACT

Several nickel-based superalloys used in the manufacture of gas turbine hot section components were investigated to determine potential alloying element effects on the uncoated alloy's resistance to low temperature hot corrosion (LTHC). In addition, the nickel-based alloy IN 738 was modified with one and two percent concentrations of hafnium to evaluate the effect of this active element on LTHC resistance.

The alloys were ranked into groups of good, moderate or poor, regarding their resistance to LTHC. Relatively high chromium contents were found to be beneficial while relatively high contents of cobalt were unexpectedly determined to be detrimental. The LTHC resistance of IN 738 was improved by small additions of hafnium.

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ACKNOWLEDGMENTS

The author is indebted to the staff of the Mechanical Engineering Department for their timely and efficient assistance and in particular to Adjunct Professor Donald H. Boone, Dr. Michael Edwards, and Mr. Tom Kellogg whose enthusiasm, help, and encouragement were instrumental in the completion of this thesis.

I. INTRODUCTION AND BACKGROUND

Hot corrosion can be regarded as an accelerated oxidation attack of metals exposed to the flow of combustion gases. It often is associated with gas turbines operating either in a marine environment, where sea salt is ingested, or with fuels containing sulphur or vanadium which can be used with turbines operated for generation of electricity. This problem is of interest to the Navy with its increased commitment to gas turbine propulsion for many of its light and medium displacement ships.

The hot section components of these turbines are constructed chiefly of nickel, cobalt, or iron-based alloys. These components, particularly the first and second stage blade and vane airfoils, are most susceptible to hot corrosion due to the temperatures to which they are exposed, and their position with respect to the combustor. Although not singularly life-limiting, hot corrosion can significantly reduce the efficiency and operational life expectancy of these components.

The contaminants which promote hot corrosion are primarily sulphur from the fuel and sea salts--in particular, sodium sulphate ingested with the combustion air. A solution would be to remove the contaminants from the fuel and filter the inlet air. Fuels used for jet aircraft gas turbines are high-cost fuels containing very small amounts of sulphur and vanadium. For ships, strategic and economic

reasons dictate the use of diesel and lower-grade fuels, and these can have higher sulphur and vanadium contents.

Compared to earlier marine gas turbines, present-day engines have more efficient multistage filtration systems built into the air intakes and consequently salt ingestion has been significantly reduced with a parallel reduction in the severity of hot corrosion. However, it is still necessary to design alloys and coatings to resist hot corrosion to further extend life and provide reliability in case of filter failure and/or inability to obtain quality fuel.

Hot corrosion is temperature dependent, and occurs over a temperature range of 593 C. to 927 C. [Ref. 1]. At temperatures below 593 C., little attack occurs because oxide scales are protective, and contaminant deposits are solid with little propensity to form deposits. Above 927 C., direct oxidation of alloys becomes more important. In the intervening temperature region, two distinct morphologies of accelerated attack occur; on this basis, hot corrosion recently has been subdivided into the high temperature (843 to 927 C.) regime and the low temperature (593 to 704 C.) regime. Corrosion morphologies observed between these two regimes are often mixtures of both types.

High temperature hot corrosion has been recognized since the 1950's. Consequently, most coatings and alloys have been designed for high temperature strength and hot corrosion and oxidation resistance. It was in 1975 that low temperature hot corrosion was recognized aboard the GTS Callagan, a test platform used to evaluate naval gas turbines [Ref. 2]. The blades used in the first stages

of the turbines aboard the Callagan were of René 80, a nickel-based superalloy coated with BC-21, an electron beam physical vapor deposition CoCrALY overlay system. The coating was selected to minimize high temperature hot corrosion. While at high power, blade temperatures were about 700 to 800 C., and hot corrosion was negligible. When the average power was reduced, blade temperatures were about 600 to 700 C., and it was found that the coatings were attacked severely. The morphology of attack (i.e., pitting of the coating) was different from that of previously reported hot corrosion, and it was gradually accepted that a low temperature form of hot corrosion existed.

Alloys and coatings rely upon protective oxides to resist hot corrosion and oxidation. These oxides generally are chromium or aluminum oxides. Chromium oxide barriers are effective against hot corrosion from low to relatively high temperatures, and aluminum oxide is very effective against high temperature hot corrosion and, of course, oxidation. It is through the breakdown of these oxides that hot corrosion attacks the substrate (or coating).

Giggins and Pettit [Ref. 3] have reviewed extensively the different mechanisms of hot corrosion. They describe hot corrosion as occurring in two stages: an initiation stage, and a propagation stage. During the initiation stage, protective oxides (such as chromium oxide or aluminum oxide) are degraded, which results in the formation of less protective oxides which are more rapidly degraded during the propagation stage.

Three different categories of propagation are presented. In the first category, the propagation stage proceeds by the mechanism determined by the alloy and the gas. This could occur on alloys with porous oxides and solids through which the gas could penetrate. In the second category, the salt, or a product of the salt-alloy-gas reaction, is required to be in the liquid phase. An example of this is the $\text{SO}_3\text{-Na}_2\text{SO}_4$ attack of virtually all alloys, depending on the partial pressure of SO_3 . In the third category, a component of salt is added to the alloy such that nonprotective reaction product barriers are formed. This can occur in the sulphur induced degradation of nickel-based alloys containing low percentages of aluminum, where the formation of sulfides prevent the growth of protective oxides. It is by a mechanism in the second category, labeled salt-fluxing reactions, that cobalt-chromium-aluminum-yttrium (CoCrALY) coatings and substrates are degraded by low temperature hot corrosion.

CoCrALY coatings were introduced in the early '70s and are the most widely used coatings on airfoils operating in a marine environment. As proposed by Giggins and Pettit [Ref. 4], the mechanism of low temperature hot corrosion attack of these coatings is summarized as follows: Hot gases containing SO_3 and deposits of Na_2SO_4 are required. Cobalt oxides react with SO_3 in the gas to form CoSO_4 which is absorbed by the Na_2SO_4 . As CoSO_4 dissolves into Na_2SO_4 , its melting point is reduced, until at 50 percent CoSO_4 there is a eutectic at 560 C. [Ref. 5]. The alloy then begins to react with components in the liquid. More specifically, oxygen is removed from the liquid salt phase. Gradients in both oxygen potential and

SO_3 are developed across the liquid with the SO_3 supplying the oxygen to react with the elements in the alloy. Aluminum is selectively removed from the alloy and is precipitated as aluminum oxide in areas of higher oxygen pressure, while chromium remaining in the aluminum-depleted zone of the alloy is converted to oxides. Cobalt dissolves in the liquid and diffuses to the outer zone of the liquid where oxides are formed, some of which are converted to sulphates and dissolved in the liquid. The morphology of this attack is characterized by chromium oxides close to the corrosion front, followed by alternating zones rich in aluminum and chromium. Cobalt oxides and sulphates are found at the corrosion product gas interface. There usually are no diffusion zones within the base alloy; this latter feature is one of the key identifying features of Type 2, low temperature hot corrosion attack.

Alloying elements are added to substrates and coatings to provide high temperature strength and hot corrosion and oxidation resistance. Unfortunately, these objectives cannot be realized simultaneously, so compromises are required to design alloys with acceptable characteristics in these respects. There is extensive literature regarding the effects of alloy additions on oxidation and high temperature hot corrosion rates. Investigators generally agree that high chromium contents are beneficial, and high aluminum and refractory metal contents are detrimental. Billingham, et. al. [Ref. 6] reported that high Ti/Al ratios are also beneficial, but additional proof is required.

Nickel-based alloys are strengthened to a large extent by gamma prime (Ni_3Al) phase precipitates. For a given chromium content alloy,

the more aluminum that is added, the greater the likelihood there is of having an alumina protective oxide formed, and thus having relatively worse hot corrosion resistance, especially if the chromium content is low. However, titanium can replace aluminum in $(\text{Ni}_3\text{Al}, \text{Ti})$. Thus, if both titanium and aluminum are involved in the formation of gamma prime, there will be less chance of the formation of an Al_2O_3 protective layer, and high temperature hot corrosion resistance may well be better.

On the other hand, there is very little information available regarding the effect of alloy additions on low temperature hot corrosion resistance. Two significant studies were reported prior to the analysis of data from the Callagan, but at that time their significance was not recognized. In 1970, Umland and Voight [Ref. 7] did studies of corrosion in alkali sulphates, and when studying cobalt and nickel alloys reported peak corrosion rates at 700 C. to 750 C. and large quantities of Co and Ni salts in the salt melt. Balajka and Daněk [Ref. 8] extended the work of Umland and Voight and observed that cobalt, through cobalt sulphates, could cause accelerated oxidation of nickel based alloys in molten alkali sulphates by a stable redox system, $(\text{Co(II)} \rightarrow \text{Co(III)})$, which can form in the salt and aid electron transfer from the alloy/melt interface to the melt/gas interface. This work had direct application to the Callagan because it implied that salt on the airfoils should be liquid, and that cobalt could affect corrosion rates.

Using a low pressure burner rig with diesel fuel in tests at 750 and 830 C., Condé, et. al. [Ref 9] noted that a series of

chromium containing alloys were more severely attacked at 750 C. than at 830 C., and that the severity of attack was related to the chromium content. The worst alloy (IN 792, 12% Cr) contained about half as much chromium as the most resistant (IN 739, 23% Cr).

Spengler [Ref. 10] reports a type of corrosion occurring in land-based turbines similar to that in marine gas turbines. This moderate temperature corrosion occurs on turbine component surfaces below 760 C., and is most severe in environments subject to sea salt contamination. As in low temperature hot corrosion, he reports that CoCrALY coatings do not appear to be sufficiently resistant to this type of corrosion, but the high Cr-Ni(Co)CrALY-family provides good resistance.

Recent coatings studies at the Naval Postgraduate School have found a strong substrate effect on the low temperature hot corrosion resistance of coatings. Specifically, it has been determined that a platinum underlayer can, in some cases, reduce LTHC attack [Refs. 11 and 12], and that small percentage additions of hafnium to a nickel-based substrate can be beneficial to a CoCrALY overlay coating. For aluminide coatings, depending on the type, Hf was found to be either beneficial or detrimental [Ref. 13].

The objective of this research is to investigate the effect of low temperature hot corrosion (704 C.) on a representative series of uncoated commercial superalloys to determine if any alloying elements have a dominant effect on low temperature hot corrosion resistance in comparison to results previously found at the higher temperatures. Also, the effect of hafnium additions on the low temperature hot

corrosion resistance of uncoated IN 738 alloys will be investigated. This information will be useful in alloy design, and will indicate if it is feasible for the Navy to use a simple furnace test, as opposed to more expensive and complicated burner rigs, in screening new alloys for relative hot corrosion resistance.

II. EXPERIMENTAL PROCEDURE

Cylindrical shaped pin specimens, approximately 0.5 cm in diameter, were used in this study. Prior to preparations for testing, experimental castings of the compositions of interest were given standard heat treatments listed in Table 1. They were then centerless ground to final shape, producing a uniform finish of about 16 uin. rms, to provide parallel surfaces to promote uniform corrosion and to facilitate measurement of metal loss due to corrosion. After cutting into specimens averaging 3.2 cm in length, the pins were inspected visually and their diameters were measured and recorded. They then were cleaned with acetone and dried prior to application of the synthetic flux. Initially, the specimens were placed into an oven preheated to 150 C. After reaching this temperature, they were sprayed with a 40 mole% MgSO_4 /60 mole% Na_2SO_4 solution. This solution was used to ensure that the salt flux was liquid at the 704 C. test temperature. At twenty minute intervals, the pins were weighed and resalted. This procedure was continued until the pins accumulated a salt coating of approximately 2 mg/cm^2 . Then they were placed into a specimen holder which was inserted into the isothermal low-temperature hot corrosion (LTHC) furnace (described in Ref. 14) with the temperature in the vicinity of the specimens maintained at 704 C. A flow of 2000 ml/min of dry air and 10 ml/min of sulphur dioxide (SO_2) gas (a 0.5% SO_2 atmosphere) was established through the LTHC furnace. These test conditions previously have been determined to produce type two, low temperature, hot corrosion in coatings [Ref. 15].

After a 20-hour exposure cycle in the above environment, the pins were removed from the LTHC furnace and allowed to air cool. After cooling, the loose scale was removed from the pins by light brushing. They then were weighed and resalted at 150 C. with a further coating of salt (of 2 mg/cm^2 as described above) and then returned to the LTHC furnace. The pins were placed in different positions in the specimen holder during each 20-hour cycle to average any potentially small temperature differences, and to achieve a uniform corrosion environment for all pins. The above procedures were repeated until a total exposure time of 100 hours in the LTHC furnace was accumulated. This produced an average surface attack of approximately 125 μm , which is consistent with present overhaul limits.

The study consisted of three Runs. Runs 1 and 2 were identical Runs designed to verify that corrosion results could be duplicated in the LTHC furnace at the Naval Postgraduate School. Run 3 was designed to investigate the potential effect of variations in concentrations of hafnium on the LTHC resistance of the alloy IN 738. The compositions of the three Runs are listed in Tables 2 and 3.

The pins then were sectioned into three pieces at approximately $1/4$, $1/2$, and $3/4$ length divisions, and prepared for microscopic evaluation using standard metallographic procedures. Diameters were measured and recorded at ten degree intervals on each section of each specimen. Two separate measurements were made on each diameter: specifically, determining metal loss, and depth of penetration. The metal loss diameters were at points where the base metal appeared

structurally sound. This measurement excluded any pits in the base metal, since a pit could be a potential stress raiser. Penetration readings measured the depth of intergranular corrosion. (This method of determining LTHC attack is illustrated in Figure 1.) The measured metal loss diameters for each section were averaged to obtain representative metal loss values for each pin. The maximum penetration readings for each specimen is the maximum penetration observed in any section of the specimen.

This method of measuring LTHC attack differs slightly from methods used elsewhere [Ref. 16] because it considers a zone of metal/corrosion products ahead of the apparently structurally useful metal, and indicates a potentially greater depth of attack than would be obtained using another method. However, this method was chosen because it recognizes the zone of metal/corrosion products and more accurately reflects the actual attack morphology.

III. RESULTS AND DISCUSSION

A. RESULTS

1. Corrosion of Runs 1 and 2

The compositions of the alloys used are listed in Table 4, and the corrosion results for Runs 1 and 2 are listed in Table 5. It can be seen that the extent of corrosion is slightly greater in Run 2 than in Run 1. Using the results of both Runs, the alloys can be qualitatively ranked as follows:

Good resistance to LTHC IN 738

IN 792

René 80

Moderate resistance to LTHC: IN 739

Nimonic 115

Poor resistance to LTHC: Udimet 700

Nimonic 105

B 1900

Three alloys exhibit minor variations in results between the two Runs:

Udimet 500: Good Run 1; moderate Run 2

IN 713 LC : Good Run 1; moderate Run 2

IN 100 : Poor Run 1; moderate Run 2

2. Corrosion of Run 3

The corrosion results of this run are listed in Table 6. These results show that small percentage additions of hafnium to IN 738 are

beneficial in terms of total depth of attack, but a change in corrosion morphology was observed and will be discussed below.

B. DISCUSSION OF RESULTS

1. Duplication of LTHC

Attacks of similar morphology as described below were noted by Condé, et. al. [Ref. 17] in 750 C. low pressure burner rig tests, and by Spengler [Ref. 18], in moderate temperature attack on land-based turbines. It has been demonstrated by Busch [Ref. 19] that the LTHC furnace used at the Naval Postgraduate School produced pitting attack on CoCrALY coatings, as described by Aprigliano [Ref. 20], using a burner rig (and as found aboard the Callagan in service, and as described by Condé [Ref. 21] using a low pressure burner rig). Therefore, it is found that the LTHC furnace at the Naval Postgraduate School can be used to study the LTHC of uncoated substrates.

2. Effect of Alloy Additions and Ranking

The ranking of the alloys generally show that high contents of chromium are associated with good LTHC resistance. This is not unexpected and confirms one of the basic rules of the design of coatings and alloys for hot corrosion that "chromium is goodness". However, high cobalt alloys tend to be worse than alloys containing about the same amount of chromium, but less cobalt. This is somewhat unexpected since one rule of thumb is that cobalt-based alloys are better than nickel-based, implying that cobalt is beneficial. The "cobalt effect" is shown by U 700, N 105, and N 115. These alloys all contain about the same amount of chromium, but U 700 and N 105

(which have higher cobalt contents) fall into the poor category, while N 115 is rated as moderate. The absence of cobalt also appears to be beneficial: IN 713 LC is rated as good or moderate, but would be expected to fall into the poor category since it has a chromium content between those of B 1900 and N 105, and a correspondingly high aluminum content with low titanium, as does B 1900 and Nimonic 105.

The detrimental effect of cobalt to LTHC resistance is consistent with the accepted mechanism of LTHC combined with the earlier findings of Umland and Voight [Ref. 22]. In the accepted mechanism, cobalt oxide on the metal surface in the presence of SO_3 gas is converted to cobalt sulfate which is absorbed by solid Na_2SO_4 deposits resulting in a melt at lower temperatures than would be possible with Na_2SO_4 alone. (In this test, the initiation stage was short-circuited by the use of a salt flux initially molten at test temperature.) Then, the additional reaction, the redox mechanism proposed by Umland and Voight (in Ref. 22) is in effect in the melt. This mechanism is based on the fact that cobalt easily can be multivalent, and that complex cobalt sulphate ions can exist in the melt. These ions then serve as electron transfer agents by oxidizing cobalt at the melt/metal interface and reducing oxygen at the melt/air interface. In the absence of a multivalent element such as cobalt, the transfer of electrons becomes more difficult. For a more detailed explanation of this mechanism, the reader is referred to Ref. 22.

The above mechanisms can then explain why this research found IN 739 to have less resistance to LTHC than Condé, et. al., and Detroit Diesel Allison [Refs. 23 and 24]. (IN 739 is a new medium strength alloy designed to provide increased hot corrosion resistance.)

It is suspected that the difference may lie in the test facilities. LTHC tests at the Naval Postgraduate School are done in the propagation stage where the salt coating of $\text{Na}_2\text{SO}_4/\text{MgSO}_4$ is liquid at 704 C., and the cobalt redox mechanism can be in effect, while other facilities are designed to operate with sea salts and simulate the intake of combustion air which takes the alloys through the initiation stage to the propagation stage. So, IN 739 could very well be good in resistance to initiation, but moderate in the resistance to attack in the propagation stage because of its high cobalt content.

It has been found in alloy development programs that to meet the creep strength requirements, a decrease in chromium content and an increase in the volume fraction of gamma prime is required. This is accomplished with higher aluminum and refractory metal contents, and lower concentrations of titanium. This combination results in poor LTHC resistance, as shown by B 1900 and Nimonic 105. However, it is difficult to separate the individual effects of chromium, titanium, and aluminum in commercial alloys since they are designed for specific service requirements involving strength, stability, cost, etc., rather than for research.

3. Variations Between Runs

This test has been shown to be extremely sensitive to variations in temperature and partial pressure of SO_3 . Busch [Ref. 25] observed a direct correlation between SO_2 input and the rate of LTHC--the rate increasing with the input of SO_2 . It is felt that minor fluctuations in one or both of these variables was responsible for

the slight differences in corrosion among the Runs and caused the variations between Runs 1 and 2.

4. Discussion of Run 3

Run 3 shows that trace additions of hafnium are beneficial in alloy IN 738; however, the morphology of attack is altered by increased amounts of intergranular corrosion. Hafnium additions to alloys are usually made for strength considerations rather than hot corrosion resistance. When added to an alloy, hafnium segregates to the grain boundary and improves intermediate temperature ductility [Ref. 26], and as reported by Edwards [in Ref. 27] there is an increase in the amount of gamma/gamma prime eutectic which improves castability. Along this line [Ref. 28], it is noted that in hafnium-enriched alloys, the morphology of the MC carbides is altered, and the gamma prime precipitates grow dendritically, resulting in a serrated grain boundary that resists sliding. These effects of hafnium on the alloy microstructure, segregated at grain boundaries and inter-dendritic areas, explain the more severe intergranular corrosion of Run 3.

The improvement in LTHC resistance is more difficult to explain. The presence of active elements such as hafnium are known to improve protective scale quality and adherence in many systems. Hafnium in the oxide also may resist basic fluxing and initial breakdown. More detailed studies of the attack morphology are required.

5. Microstructure Examination

The typical attack morphology observed is characterized by a layer of oxides, then a zone of corrosion products/base metal, followed by a sound-base metal. There appears to be no layer in the base metal where the alloy is depleted, and there is no evidence of localized pitting. This latter point is significant in comparison with CoCrALY coatings where the apparent pitting nature of the attack is related to the initial quality of the oxide (Al_2O_3), where local penetration results in a pit-like attack. Without the presence of this oxide, or in the case of the uncoated alloy, the attack is much more uniform.

Micrographs from Run 1 of René 80, Nimonic 115, and Nimonic 105 are shown in Figure 2. These alloys were ranked good, moderate, and poor, respectively. There are no visual correlations which relate LTHC resistance and physical appearance of attack. For all systems, the transition from the corrosion product/alloy zone to the sound base alloy is distinctive.

Figures 3 and 4 show micrographs from Runs 1 and 2 of IN 100 and IN 713 LC, alloys in which variations in ranking occurred between runs. The morphology of attack between the two runs is consistent. There are no apparent differences in the micrographs to account for the variations between runs.

Typical micrographs from Run 3 for IN 738, IN 738 + 1% Hf, and IN 738 + 2% Hf are shown in Figures 5, 6, and 7. The attack morphology in the corrosion product/base metal zone is similar in all the micrographs, but more intergranular corrosion is apparent

in the alloy plus hafnium micrographs. Disregarding the greater intergranular corrosion attack, the morphology of attack in this Run essentially is the same as that in Runs 1 and 2.

IV. CONCLUSIONS AND RECOMMENDATIONS

Based on results from the three experimental Runs using the isothermal resistance furnace, the following conclusions are summarized from the preceding chapters:

1. The LTHC resistance furnace test at the Naval Postgraduate School is capable of reproducing Type 2 hot corrosion attack on uncoated alloys as well as coatings.

2. Relatively high chromium contents are beneficial regarding the LTHC resistance of uncoated alloys.

3. High cobalt concentrations appear to be detrimental to the LTHC resistance of uncoated alloys, and can detract from, or interfere with, the beneficial effects of chromium.

4. Additions of the active element hafnium to IN 738 have a beneficial effect on the resistance of the uncoated alloy to LTHC--the optimum concentration being about one percent.

It is difficult to determine the effect of individual alloy elements in the LTHC studies using commercial alloys due to the complexity of these systems. Simple systems should be studied to obtain more explicit information. Along this line of reasoning, the following recommendations for future research are offered:

1. Design a study using a series of alloys with variations in chromium and cobalt contents with a constant concentration of aluminum so the individual effects of these elements on the LTHC resistance of uncoated alloys may be more closely investigated.

2. Titanium is an important element because it has been found to be detrimental to coatings. No assessment of the effect of titanium could be made from this study. Therefore, a study of a simple series of alloys with variations in the concentration of titanium should be conducted to determine its effect in uncoated alloys.

APPENDIX A: TABLES 1-6

TABLE 1

HEAT TREATMENTS OF SUPERALLOYS USED IN RUNS 1, 2 AND 3

IN 739	4 hrs @ 1150 C., air cool
	6 hrs @ 1000 C., air cool
	24 hrs @ 900 C., air cool
	16 hrs @ 700 C., air cool
Udimet 700:	4 hrs @ 1175 C., air cool
	4 hrs @ 1080 C., air cool
	24 hrs @ 843 C., air cool
	16 hrs @ 760 C., air cool
Nimonic 115:	1.5 hrs @ 1190 C., air cool
	6 hrs @ 1098 C., air cool
Nimonic 105:	4 hrs @ 1150 C., air cool
	16 hrs @ 1060 C., air cool
	16 hrs @ 850 C., air cool
René 80:	2 hrs @ 1218 C., air cool
	4 hrs @ 1093 C., air cool
	4 hrs @ 1050 C., furnace cool
	16 hrs @ 845 C., air cool
	16 hrs @ 760 C., air cool
IN 792, IN 738:	2 hrs @ 1120 C., air cool
	24 hrs @ 845 C., air cool
Udimet 500:	4 hrs @ 1150 C., air cool
	4 hrs @ 1080 C., air cool
	16 hrs @ 760 C., air cool
B 1900, IN 100, IN 713 LC:	4 hrs @ 1080 C., air cool

TABLE 2

ALLOYS USED IN EXPERIMENTAL RUNS 1 AND 2

Alloy	Run 1	Run 2
	Average Diameter (mm)	Average Diameter (mm)
Nimonic 115	6.911	5.646
IN 713 LC	6.944	5.639
IN 792	6.911	5.631
IN 739	6.911	5.618
IN 100	6.944	5.636
B 1900	6.916	5.685
René 80	6.871	5.652
IN 738	6.927	5.601
Nimonic 105	6.957	5.644
Udimet 700	6.960	5.626
Udimet 500	6.371	5.649

TABLE 3

ALLOYS USED IN EXPERIMENTAL RUN 3

Alloy	Average Diameter (mm)
IN 738	5.814
IN 738	5.596
IN 738	5.585
IN 738	5.667
IN 738 + 1% Hf	5.461
IN 738 + 1% Hf	5.461
IN 738 + 1% Hf	5.636
IN 738 + 1% Hf	5.603
IN 738 + 2% Hf	5.489
IN 738 + 2% Hf	5.484
IN 738 + 2% Hf	5.591
IN 738 + 2% Hf	5.631

TABLE 4
CHEMICAL COMPOSITIONS OF ALLOYS USED IN RUNS 1, 2 AND 3

Alloy	Alloy Elements (wt. %)												
	Ni	C	Cr	Co	W	Mo	Ta	Al	Ti	Nb	B	Zr	V
IN 739	48.2	0.15	22.5	19.0	2.0	--	1.4	1.9	3.7	1.0	0.011	0.10	--
IN 100	59.5	0.18	10.0	15.0	--	3.0	--	5.5	4.7	--	0.014	0.06	1.0
IN 738	61.4	0.17	16.0	8.5	2.6	1.75	1.75	3.4	3.4	0.9	0.010	0.10	--
IN 792	60.8	0.21	12.7	9.0	3.9	2.0	3.9	3.2	4.2	--	0.020	0.10	--
N 115	57.4	0.15	15.0	15.0	--	3.5	--	5.0	4.0	--	--	--	--
Rene' 80	60.3	0.17	14.0	9.5	4.0	4.0	--	3.0	5.0	--	0.015	0.03	--
B 1900	64.5	0.1	8.0	10.0	--	6.0	4.3	6.0	1.0	--	0.015	0.08	--
U 500	53.6	0.08	18.0	18.5	--	4.0	--	2.9	2.9	--	0.005	0.05	--
U 700	53.4	0.08	15.0	18.5	--	5.2	--	4.3	3.5	--	0.030	--	--
IN 713 LC	74.8	0.05	12.0	--	--	4.5	--	5.9	0.6	2.0	0.010	0.10	--
N 105	54.6	0.2	14.5	20.0	--	5.0	--	4.7	1.2	--	--	--	--

TABLE 5

CORROSION RESULTS RUNS 1 AND 2

Alloy	Run 1			Run 2		
	Metal Loss* um (Mils)	Max. Penetration* um (Mils)	Alloy	Metal Loss* um (Mils)	Max. Penetration* um (Mils)	
Udimet 500	81.3 (3.2)	142.2 (5.6)	IN 738	104.1 (4.1)	175.3 (6.9)	
IN 713 LC	83.8 (3.3)	170.2 (6.7)	Rene 80	111.8 (4.4)	182.9 (7.2)	
IN 792	88.9 (3.5)	188.0 (7.4)	IN 792	142.2 (5.6)	193.0 (7.6)	
Rene' 80	116.8 (4.6)	188.0 (7.4)	IN 100	154.9 (6.1)	246.4 (9.7)	
IN 738	119.4 (4.7)	210.8 (8.3)	Nimonic 115	162.6 (6.4)	238.8 (9.4)	
IN 739	119.4 (4.7)	185.4 (7.3)	IN 739	167.6 (6.6)	315.0 (12.4)	
Nimonic 115	129.5 (5.1)	215.9 (8.5)	IN 713 LC	180.3 (7.1)	269.2 (10.6)	
Udimet 700	144.8 (5.7)	195.6 (7.7)	Udimet 500	203.2 (8.0)	294.6 (11.6)	
Nimonic 105	147.3 (5.8)	213.4 (8.4)	Nimonic 105	221.0 (8.7)	342.9 (13.5)	
B 1900	167.6 (6.6)	236.2 (9.3)	Udimet 700	238.8 (9.4)	315.0 (12.4)	
IN 100	185.4 (7.3)	241.3 (9.5)	B 1900	304.8 (12.0)	388.6 (15.3)	

*Metal loss and penetration on a radius.

TABLE 6

CORROSION RESULTS FOR RUN 3

Alloy	Metal Loss*		Maximum Penetration*	
	(μ m)	(Mils)	(μ m)	(Mils)
IN 738	165.1	(6.5)	264.2	(10.4)
IN 738	172.7	(6.8)	231.1	(9.1)
IN 738	154.9	(6.1)	228.6	(9.0)
IN 738	149.9	(5.9)	299.7	(11.8)
IN 738 + 1% Hf	149.9	(5.9)	226.1	(8.9)
IN 738 + 1% Hf	152.4	(6.0)	243.8	(9.6)
IN 738 + 1% Hf	132.1	(5.2)	200.7	(7.9)
IN 738 + 1% Hf	129.5	(5.1)	200.7	(7.9)
IN 738 + 2% Hf	149.9	(5.9)	221.0	(8.7)
IN 738 + 2% Hf	139.7	(5.5)	210.8	(8.3)
IN 738 + 2% Hf	139.7	(5.5)	281.9	(11.1)
IN 738 + 2% Hf	170.2	(6.7)	254.0	(10.0)

AVERAGE RESULTS

Alloy	Metal Loss*		Maximum Penetration*	
	(μ m)	(Mils)	(μ m)	(Mils)
IN 738	160.7	(6.3)	255.9	(10.1)
IN 738 + 1% Hf	141.0	(5.6)	217.8	(8.6)
IN 738 + 2% Hf	149.9	(5.9)	241.9	(9.5)

* Metal Loss and Maximum Penetration on a Radius.

APPENDIX B: FIGURES 1-7

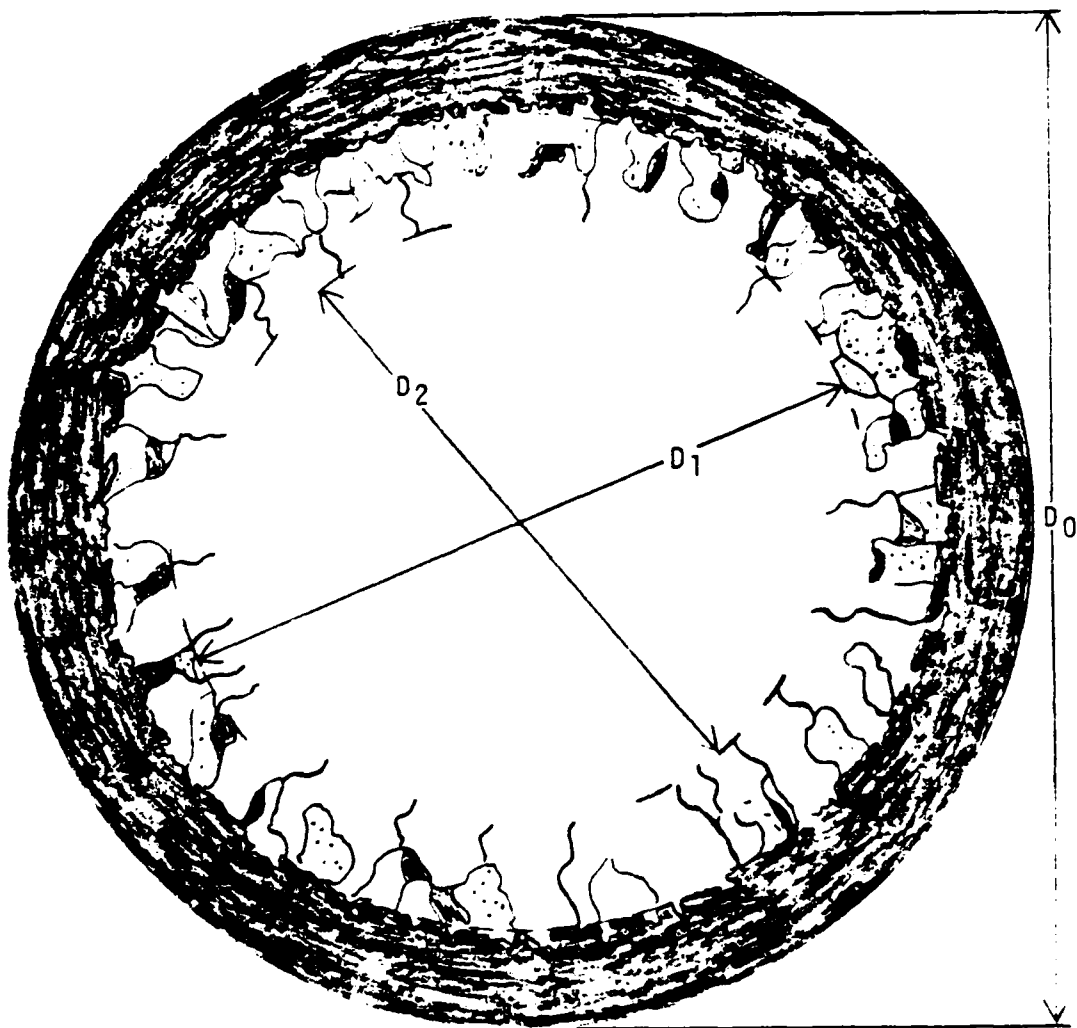
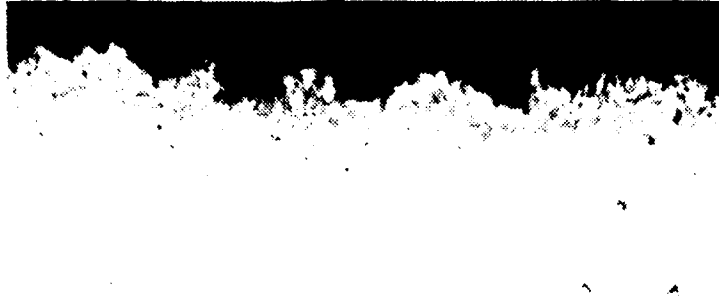
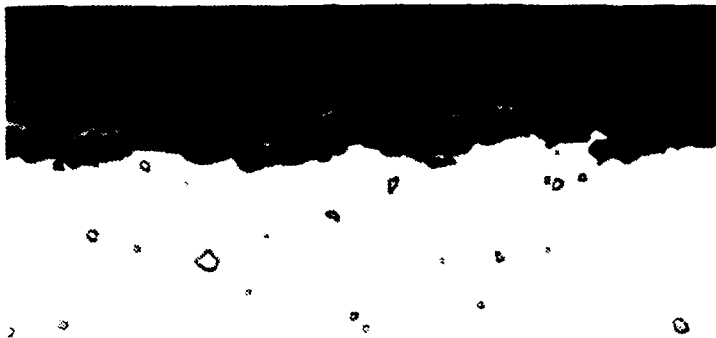


Figure 1: Method of Measuring Metal Loss and Maximum Penetration of alloys subjected to LTHC.

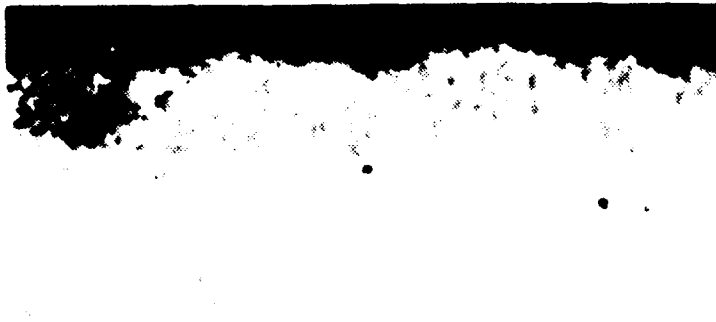
- D_0 : Original metal diameter measured with a micrometer.
- D_1 : Metal loss reading measured at the transition from corrosion product/base metal zone to sound base metal.
- D_2 : Maximum penetration measurement based on depth of inter-granular corrosion.



(a)



(b)



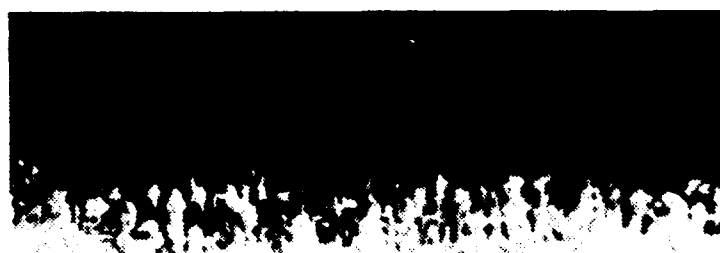
(c)

Figure 2: Photomicrographs of alloys from Run 1.

400x unetched photomicrographs of René 80 (a), Nimonic 115 (b), and Nimonic 105 (c) from Run 1, ranked good, moderate, and poor respectively. Note the similar attack morphologies for the three rankings and the distinct transition from the corrosion product/base metal zone to sound base metal.



(a)



(b)

Figure 3: Photomicrographs of IN 713 LC from Runs 1 and 2.

400x, unetched photomicrographs of IN 713 LC from Run 1 (a) and Run 2 (b), alloys in which variations occurred between the runs. Note the consistency of the morphology of attack between the two runs.



(a)



(b)

Figure 4: Photomicrographs of IN 100 from Runs 1 and 2.

400x, unetched photomicrographs of IN 100 from Run 1 (a) and 2 (b), alloys in which variations occurred between the runs. Note the consistency of the morphology of attack between the two Runs.

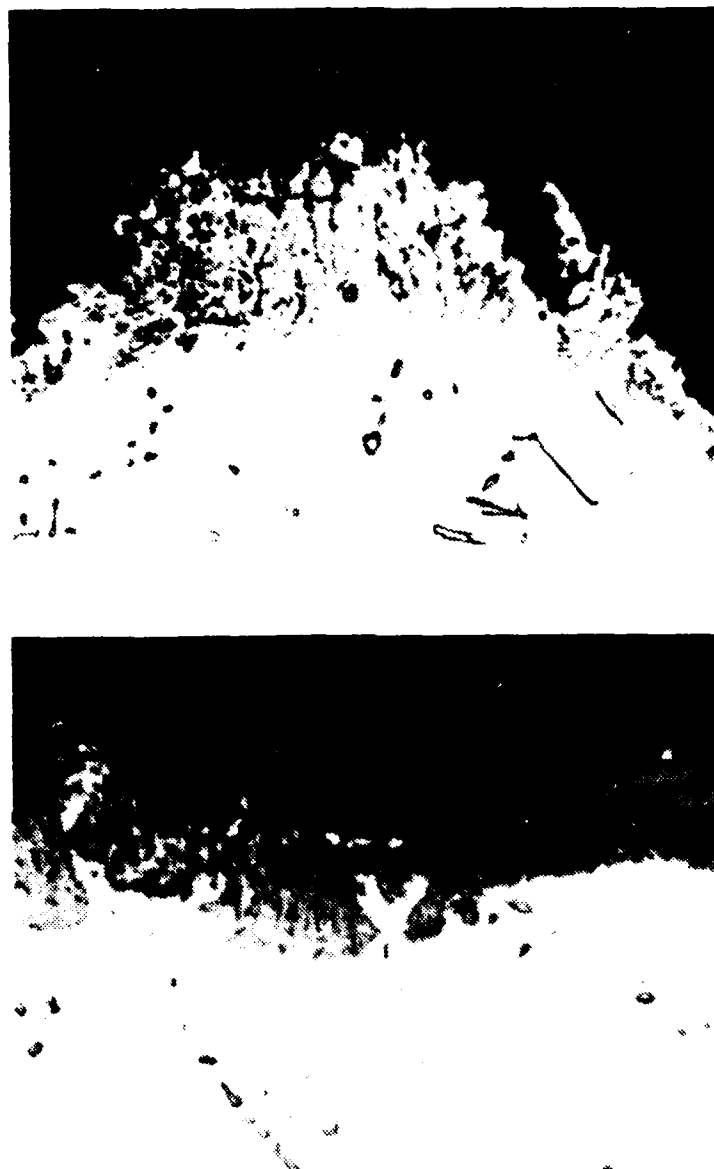


Figure 5: Photomicrographs of LTIC attack of IN 738 containing no Hf. (Run 3).

400x, unetched photomicrographs of IN 738 containing no Hf from Run 3. Note the morphology of attack is similar to that of Runs 1 and 2. (Figures 2 and 3)

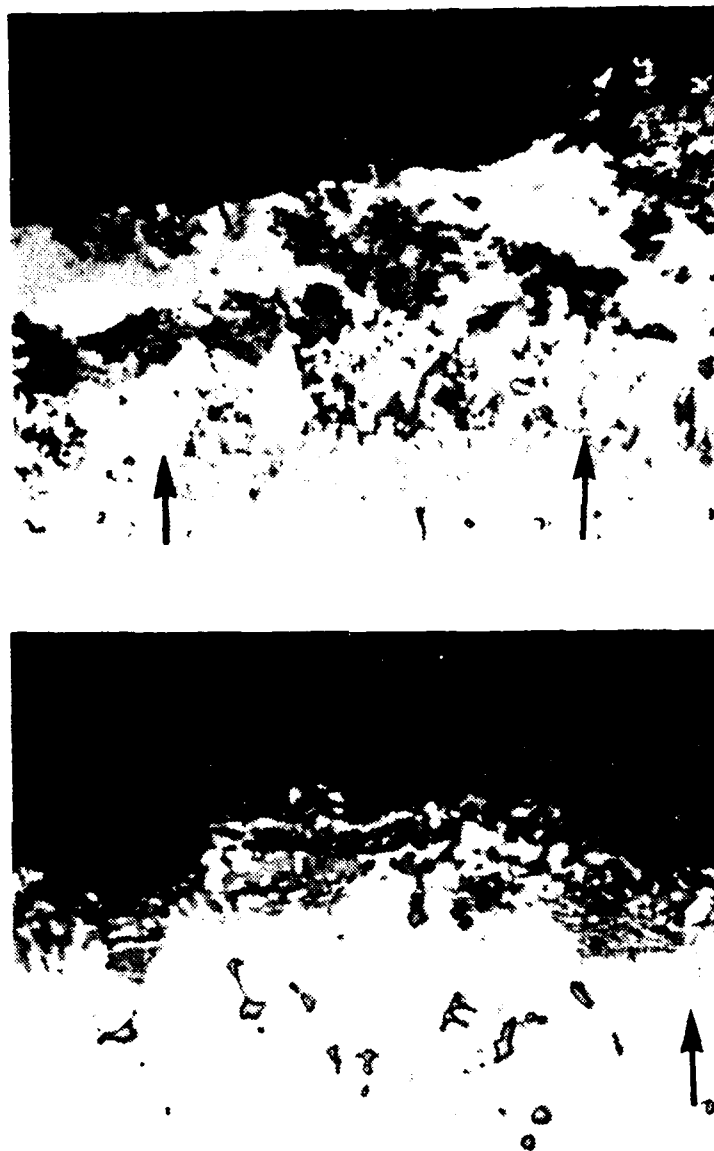


Figure 6: Photomicrographs of LTHC attack of IN 738 + 1% Hf (Run 3).

400 x, unetched photomicrographs of IN 738 + 1% Hf. Note the intergranular corrosion (arrows) and similar attack morphology to that of Runs 1 and 2. (Figures 2 and 3.)

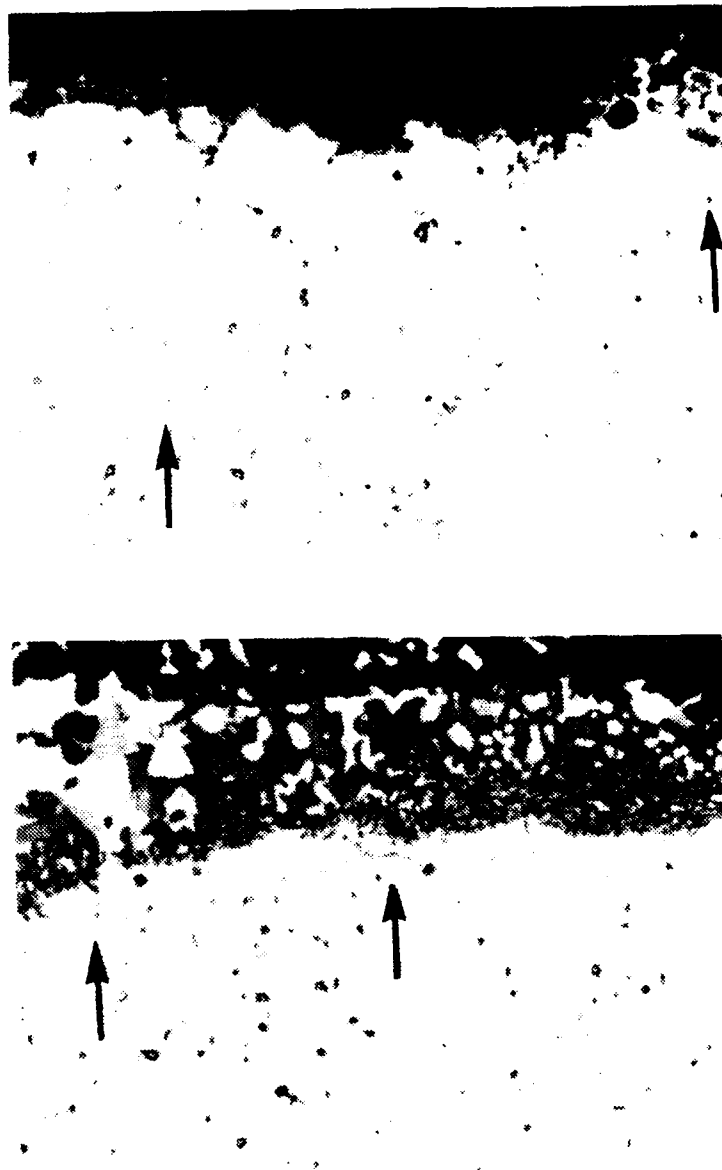


Figure 7: Photomicrographs of LTHC attack of IN 738 + 2% Hf. (Run 3).

400 x, unetched photomicrographs of IN 738 + 2% Hf. Note the intergranular corrosion (arrows), and the similar attack morphology to that of Runs 1 and 2 (Figures 2 and 3).

LIST OF REFERENCES

1. Aprigliano, L. F., Low and High Temperature (1300° and 1650°F) Burner Rig Tests of MCrAlY Composition Variations, paper presented at the Gas Turbine Materials in a Marine Environment Conference, 4th, Annapolis, MD, 26 June 1979.
2. Naval Research Laboratory Memorandum, Report 4072, A Summary and Review of Navsea Funded Low Power Hot Corrosion Studies, by R. L. Jones, p. 2, 24 September 1979.
3. Pratt and Whitney Aircraft Group, United Technologies Corporation, Report FR-11545, Hot Corrosion Degradation of Metals and Alloys--A Unified Theory, by C. S. Giggins and F. S. Pettit, June 1979.
4. Ibid., pp. 35-37.
5. Luthra, K. L. and Shores, D. A., Morphology of Na₂SO₄ Induced Hot Corrosion at 600°-750°C, paper presented at the Gas Turbine Materials in a Marine Environment Conference, 4th, Annapolis, MD, 26 June 1974.
6. Billingham, J., Lauridsen, J., Lawn, R. E., and Dewey, A. A. P., in C.E.G.B. Conference on Corrosion and Deposition in Gas Turbines, Proceedings (A. B. Hart and A. J. S. Cutler, eds.), pp. 229-43, Applied Science Publishers, Essex, England, 1973.
7. Umland, F. and Voight, H. P., "Die Polle der Alkalisulfate bei der Hochtemperatur Korrosion", Werkstoffe und Korrosion, V-21, pt. 4, pp. 254-63, 1970.
8. Balajka, J. and Daněk, V., "Corrosion of Ni in Molten Alkali Sulfates", Werkstoffe und Korrosion, V. 25, pt. 7, pp. 513-21, 1974.
9. Taylor, A. F., Wareham, B. A., Booth, G. C. and Conde, J. F. G., Low and High Pressure Rig Evaluation of Materials and Coatings, paper presented at the Conference on Gas Turbines in a Marine Environment, 3rd, University of Bath, England, 22 September 1976.
10. Spengler, C. J., in Superalloys 1980, Proceedings, (John K. Tien, Stanley I. Wlodek, Hugh Morrow III, Maurice Gell and Gernant E. Maurer, eds.), pp. 395-404, American Society for Metals, Cleveland, Ohio, 1980.

11. Busch, D. E., The Platinum Effect in the Reduction of Low Temperature Hot Corrosion on Marine Gas Turbine Materials, Master's Thesis, Naval Postgraduate School, Monterey, CA, December 1979.
12. King, R. H., An Investigation of the Substrate/Platinum Effect in Low Temperature Hot Corrosion of Marine Gas Turbine Materials, Master's Thesis, Naval Postgraduate School, Monterey, CA, June 1981.
13. Exell, J. R., The Substrate Effect of Active Element Hafnium in Aluminide Coatings, Master's Thesis, Naval Postgraduate School, Monterey, CA, June 1981.
14. Busch, D. E., op. cit.
15. Ibid.
16. Detroit Diesel Allison Report No. 9468A, Development of Improved Marine Gas Turbine Airfoils Using Directional Solidification, by R. C. Benn, H. F. Merrick, S. W. K. Shaw, K. A. Green and E. S. Nichols, p. 14, 14 December 1978.
17. Taylor, A. F., et. al., op. cit.
18. Spengler, C. J., op. cit.
19. Busch, E. E., op. cit.
20. Aprigliano, L. F., op. cit.
21. Taylor, A. F., et. al., op. cit.
22. Umland, F. and Voight, H. P., op. cit.
23. Taylor, A. F., et. al., op. cit.
24. Detroit Diesel Allison Report No. 9468A, p. 1, op. cit.
25. Busch, D. E., op. cit.
26. Ouichou, L., Lavaud, F. and Lesoult, G., in Superalloys 1980, Proceedings, (John K. Tien, Stanley T. Wlodek, Hugh Morrow III, Maurice Gell and Gernant E. Maurer, eds.), pp. 235-44, American Society for Metals, Cleveland, Ohio, 1980.
27. Edwards, Michael R., in Superalloys 1980, Proceedings, (John K. Tien, Stanley T. Wlodek, Hugh Morrow III, Maurice Gell and Gernant E. Maurer, eds.), pp. 295-301, American Society for Metals, Cleveland, Ohio, 1980.
28. Copley, S. M., Williams, C. J., et. al., Alloy and Microstructure Design, p. 34, Academic Press, Inc., 1976.

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